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Study of novel solvent for CO_2 post-combustion capture

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Abstract

Carbon dioxide post-combustion capture process using an aqueous solution of 30 wt% of monoethanolamine (MEA) is considered the most mature solution for CO_2 removal from bulk CO_2 gas streams. Although this amine based process is considered mature and has good performance characteristics such as good CO_2 absorption and high kinetics; it has high energy requirement which is approximately 3.6-4 GJ/ton of CO_2. This high energy demand is the driving force behind the research activities seeking novel solvents with lower energy consumption. This work focuses on the thermodynamic and kinetics characterization of new amine-based solvents to evaluate their potential for CO_2 removal. A screening of different amines structure was done for the determination of the CO_2 loading by using solvent screening setup (S.S.S.) at 313.15K and a pressure of 1 bar containing 15 %vol CO_2 and 85 %vol N_2. For the evaluation of the heat of absorption, a micro-reaction calorimeter was used at 313.15K and atmospheric pressure with pure CO_2. The kinetics properties were obtained with stopped-flow equipment to measure the pseudo-first order reaction k_0 (s^{-1}) at 298.15, 303.15, 308.15 and 313.15K. The results show that two tertiary amines, 2-(dimethylamino)ethanol (2DMEA) and 3-dimethylamino-1-propanol (3DMA1P), have high potential to blend with primary or secondary amine in order to improve the CO_2 loading, the heat of absorption and the reaction kinetics instead of using MDEA.

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Keywords: monoethanolamine, CO_2 loading, heat of absorption, kinetics.

1. Introduction

Alkanolamines-based processes are the most studied solution for CO_2 post-combustion capture applications. These alkanolamines include the primary amines (MEA – monoethanolamine), secondary amines (DEA – diethanolamine) and tertiary amines (MDEA- N-methyldiethanolamine) [1-5]. The primary and secondary alkanolamines react faster with carbon dioxide with the formation of carbamate species. The heat of absorption of this reaction is very high and increase the required regeneration energy

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of the solvent. The maximum theoretical CO_2 loading of the primary and secondary amines is 0.5 mole of CO_2/mole of amine (two molecules of amines is needed to react with one molecule of CO_2). The CO_2 loading of the tertiary alkanolamines is higher with a maximum of 1 mole of CO_2 per mole of amine; one molecule of amine react with one molecule of CO_2 and this reaction does not form carbamate but it forms bicarbonates. The tertiary alkanolamines reactivity with CO_2 is lower in comparison with the primary or secondary amines. Thus, the heat of absorption associated with this reaction is lower and the energy required to regenerate the amine solvent will be reduce.

Aqueous solution of MEA 30 wt% is the most mature solution for CO_2 post-combustion capture. However, the energy of regeneration of this solvent is very high [6-7]. To overcome this process problem, various methods have been considered. Previous works studied different amines (linear, cyclic, polyamines…) in order to establish a relation between the structure of the amine and the thermodynamic properties [8-10]. The published results show the potential of the modification of the structure in order to find some promising amine for CO_2 capture. Recent studies have focused on sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP). This class of amine has their amino group attached into a large group (e.g. ethyl, butyl, t-butyl…). Due to the presence of this group, the formed carbamate is unstable and instantly transformed to bicarbonate, which results in a maximum CO_2 loading of 1 mole of CO_2 per mole of amine [11-12]. Beside the exploration of amine structure to reduce the heat of absorption, amine blends are also used to optimize the properties of the absorbent by combining the performance advantages of each amine in the newly blended solvent (e.g. high CO_2 loading from tertiary amines and fast absorption rates from primary or secondary amines) [13-17].

The aim of this work is to characterize new amine solvents to evaluate its possibility to develop novel amine blends for CO_2 capture application in order to reduce the energy of regeneration process with reasonable kinetics and CO_2 absorption capacity. CO_2 loading capacity, heat of absorption and CO_2-amine reaction kinetics will be determined and then used as the major parameters for the single amine selection. The results obtained from this research will be the basis for the later development of novel amine blends.

Nomenclature

k_0	pseudo-first order rate constant (s^{-1})
ΔH	enthalpy of reaction (kJ/mol of CO_2)
s	second
mW	power
Y	conductance (S)
A	amplitude of signal (S)
t	time
Y_∞	conductance of the end of observed reaction (S)
α	CO_2 loading
k_2	second order rate constant ($m^3.mol^{-1}.s^{-1}$)
E_A	Activation energy ($kJ.mol^{-1}$)
A_1	Arrhenius constant ($m^3.mol^{-1}.s^{-1}$)
R	molar gas constant ($J.K^{-1}.mol^{-1}$)

T	temperature (K)

2. Experimental section

2.1. Materials

All amines used in this work were purchased from Sigma Aldrich (purity ≥99 %). The aqueous amine solutions were prepared by dilution of amine solvent with distilled water. CO_2 (≥99.5%) and N_2 (≥99%) were used to simulate the flue gas in the experiments. The details of the chemicals used in this work are reported in appendix A.1.

2.2. Solvent screening setup (S.S.S.) for CO_2 absorption

A full description of the solvent screening setup can be found in the previous work of the authors [6]. The setup has six parallel glass reactors (250 mL ± 0.5) operational in the temperature range from 298.15 K to 423.15 K (± 1 K) and the pressure range of 0-6 bars (± 0.01 bar). A magnetic stirrer is used in order to ensure a homogeneous contact between the solution and CO_2 by creation of a vortex (maximum speed is 1500 rpm (± 1 rpm)). In each experiment, 150g of aqueous amine solution 30 %wt were prepared and transferred to the reactors. The absorption was conducted at 313.15 K with the mixing speed at 500 rpm. A mixture of CO_2 and N_2 (15 Vol% and 85 Vol%, respectively) was initially fed to a make-up vessel until a pressure of 2 bars is achieved and then it was flown into the each reactor by controlling a mass flow controller at a flow rate of 15 L/h. The total pressure inside reactors was kept at 1 bar throughout the absorption experiment. The reaction of CO_2 with the solution will be completed when equilibrium is reached. To prevent solvent loss, a condenser was used at a temperature of 279.65 K.

2.3. Phosphoric acid titration (P.A.T.) for determination of CO_2 loading

PAT is a titration set up used to determine the CO_2 loading in the rich aqueous amine solution. A round-bottom flask with 85% of phosphoric acid solution was used. Temperature is controlled by using a heating mantle (maximum temperature of 673.15K). Phosphoric acid reacts with rich CO_2 loaded amine at 453.15 K to desorb CO_2 from the aqueous amine solution. A flow of nitrogen is used in order to sweep the CO_2 from the system. The CO_2/N_2 gas mixture passes through a CO_2 infrared analyser in order to obtain the amount of CO_2 released from the amine-H_2O-CO_2 system. The software shows the amount of CO_2 in % over the time. Experiment was repeated three times for verification of the amount of CO_2 loading. CO_2 loading was calculated by:

$$\alpha_{CO2} = \frac{n_{CO2}}{n_{amine}} \quad (1)$$

2.4. Micro-reaction calorimeter for determination of heat of absorption

A flow micro-reaction calorimeter supplied by thermal Hazard Technology (UK) was used to evaluate the heat of absorption of aqueous amine solution (enthalpy of reaction – ΔH (kJ/mol of CO_2)). The system can operate at temperature from 298.15 to 353.15 K (± 1 K) and flow gas can be adjusted from 0 to 20 ml/min (± 0.1 ml/min). The calorimeter is controlled by a URC control software provided by Thermal Hazard Technology. In a typical experiment, the cell containing sample was placed into the calorimeter and temperature was set at 313.15 K at atmospheric pressure. As the experiment starts, the variation of

power (mW) with time (s) was recorded by the software. When the signal is stable, CO_2 gas was introduced into the cell with a rate of 0.5 ml/min (± 0.01 ml/min). CO_2 flow, which is controlled by mass flow controller, goes through a desiccant column in order to remove moisture before entering into the sample cell. Because the reaction of CO_2 with aqueous amine solution is exothermic, the power signal initially increases and then, the signal decrease and became constant when the reaction is completed (equilibrium). Sample weight before and after the absorption of CO_2 was checked in order to know the mass of CO_2 absorbed. This value was used to determine the CO_2 loading as the equation (1). The integral heat Q (in J) was determined by using the URC software. Finally, the heat of absorption (ΔH - kJ/mole of CO_2) was calculated by the division of the integral heat Q by the mole of CO_2 absorbed.

2.5. Stopped-flow equipment for the determination of the kinetics

In order to investigate the kinetics of absorption of CO_2 by an aqueous amine solution, a stopped-flow meter (SF-61SX2) supplied by TgK Scientific suppliers of Hi-Tech Scientific Instruments, UK, was used. First, an aqueous solution of CO_2 was prepared by bubbling this gas during approximately 2 hours in distilled water at a temperature of 298.15 K and atmospheric pressure. Then, different concentration of amine was prepared in the range permit for the stopped-flow equipment. For each amine concentration, a concentration of CO_2 was prepared by dilution of the stock solution in order to keep CO_2 solution at approximately 15 times lower than aqueous amine solution. The amine solution and the corresponded CO_2 solution are then introduced to reactant containing cylinders by using syringes. The water jacket used with a bath permit to have a homogeneous constant temperature for the solution. Then, a pneumatic drive plate pushes the two fresh solution in equal volume into a mixing conductivity cell in order to make the reaction between aqueous CO_2 solution and aqueous amine solution. The change in voltages will be converted to the change in conductivities of the solution by the calibrated cell voltage with the conductivities of the standard potassium chloride (KCl) solution. The experimental evolution of the conductivity with the time was fitted by using the exponential equation below and the software calculates the pseudo-first rate constant k_0 (s^{-1}) (Eq. 2):

$$Y = -A \exp(-k_o t) + Y_\infty \quad (2)$$

Where Y is the conductance (S), A is the amplitude of the signal (S), k_0 is the pseudo-first order reaction rate constant (s^{-1}), t is the time (s) and Y_∞ is the conductance of the end of observed reaction (S).

3. Results and discussions

3.1. Absorption of CO_2

Table 1 shows the CO_2 loading of aqueous amine solution 30 wt% at 313.15K and P_{CO2}=0.15bar. The data revealed that DAP and HMD, which contains two nitrogen, have the highest CO_2 loading (1.23 mole CO_2/mole amine and 1.35 mole CO_2/mole amine, respectively) among all tested amines. For the amines which contains one nitrogen in their chemical structure, 3DMA1P and DEEA have the highest CO_2 absorption capacity (0.89 mole CO_2/mole amine and 0.90 mole CO_2/mole amine, respectively). Moreover, although 2TBAE is a secondary amine, the measured CO_2 absorption (0.87 mole CO_2/mole amine) was found high and close to the values of 3DMA1P and DEEA.

Table 1. CO_2 loading of aqueous amines solution at 313.15 K and P_{CO2}=0.15bar.

	Amines	Concentration (wt%)	α_{CO2}
1	Monoethanolamine (MEA)	30	0.58
2	1-amino-2-propanol (1A2P)	30	0.54
3	2-amino-1-butanol (2A1B)	30	0.59
4	2-amino-1-methyl-2-propanol (AMP)	30	0.80
5	2-(tert-butylamino)ethanol (2TBAE)	30	0.87
6	2-(dimethylamino)ethanol (2DMAE)	30	0.73
7	N,N-diethylethanolamine (DEEA)	30	0.90
8	N-methyldiethanolamine (MDEA)	30	0.52
9	Triethanolamine (TEA)	30	0.39
10	Sec-butylamine (SBA)	30	0.70
11	Isobutylamine (IBA)	30	0.59
12	3-dimethyl-amino-1-propanol (3DMA1P)	30	0.89
13	1,3-diaminopropane (DAP)	30	1.23
14	Hexamethylenediamine (HMD)	30	1.35

If we consider MEA structure as a basic unit, then the other amines would be obtained by adding functional groups to the unit. The addition of functional groups to MEA structure may cause a significant effect on the CO_2 absorption performance of the amines. The modifications on the MEA structure and their impact on the CO_2 loading are shown in Fig. 1, Fig. 2 and Fig. 3.

1A2P has a methyl group attach to the first carbon near the alcohol group and 2A1B has an ethyl group attached to the first carbon near the nitrogen site (Fig. 1). The CO_2 loading values of these two amines suggest that the ethyl and methyl group do not have strong effect on the CO_2 absorption (Table 1). In comparison with MEA, AMP and 2TBAE comprises two methyl attached to the first carbon near the nitrogen and one t-butyl group replacing hydrogen attached to the nitrogen site. The presence of these groups increase the CO_2 loading from 0.58 mole CO_2/mole amine for MEA to 0.80 mole CO_2/mole amine for AMP and from 0.58 mole CO_2/mole amine for MEA to 0.87 mole CO_2/mole amine for 2TBAE. The results obtained in this study display that the presence of carbon group in the nitrogen is benefit in order to have a high CO_2 absorption.

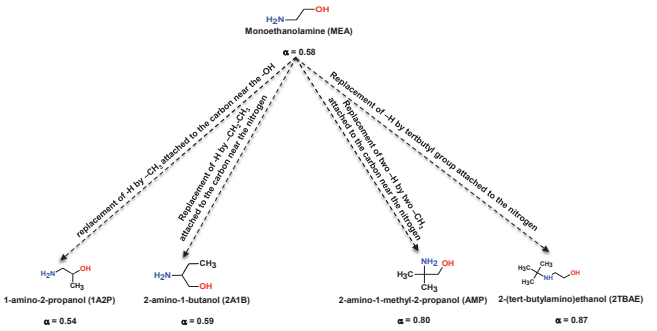

Fig. 1. Modification of the chemical group from MEA structure.

From MEA, two hydrogen of the nitrogen site were replaced by two methyl to obtain 2DMAE (Fig. 2). The effect of this chemical modification show a highest CO_2 loading when the methyl group are present (0.73 mole CO_2/mole amine). The substitution of the two hydrogen attached to the nitrogen of MEA by two ethyl (DEEA) increase significantly the CO_2 absorption from 0.58 mole CO_2/mole amine to 0.90 mole CO_2/mole amine. Moreover, the change of the two methyl present in the nitrogen site for 2DMAE by two ethyl group to obtain DEEA increase also the CO_2 loading. The effect of alcohol group into CO_2 loading is presented. In comparison with 2DMAE, the two hydrogen of the nitrogen site were substituted by one methyl and one alcohol group in order to obtain MDEA. The result show that the CO_2 loading of MDEA is lower than MEA which is lower than 2DMAE. While three alcohol group is attached to the nitrogen (TEA), the CO_2 loading decrease and a value of 0.39 mole CO_2/mole amine was found. These results show that methyl or ethyl attached to the nitrogen increase the CO_2 absorption of the molecule more than hydrogen or alcohol group.

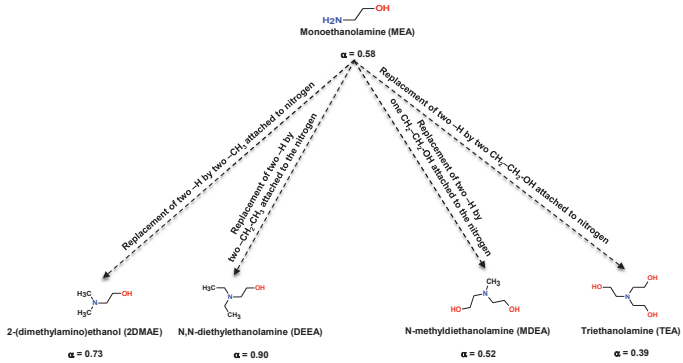

Fig. 2. Modification of the chemical group from MEA structure to obtain tertiary amine.

Fig. 3 show the effect when the alcohol of MEA is substituted by a methyl and the hydrogen of the first carbon and second carbon from nitrogen is replaced by a methyl to obtain SBA and IBA respectively. From MEA structure, the CO_2 loading values show that the modification of the structure in order to obtain SBA and IBA have a strong impact for SBA and no impact for IBA. Moreover, SBA absorb more CO_2 than IBA (0.70 against 0.59 mole CO_2/mole amine) because of the presence of methyl near the nitrogen, for SBA, which increase the basicity of the nitrogen.

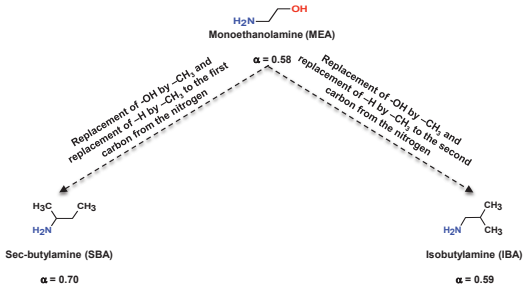

Fig. 3. Substitution of alcohol by methyl and modification of the chemical group from MEA structure.

A second effect concerning the relation between the amine structure and the CO_2 loading is shown in this work (Fig. 4). The influence of the chain length to the CO_2 absorption between 2DMAE and

3DMA1P is shown in Table 1. Results show that increase the chain length from two carbon (2DMAE) to three carbon (3DMA1P), will increase the CO_2 loading increase from 0.73 to 0.89 mole CO_2/mole amine. This difference is due to the distance between the alcohol group and the nitrogen site. More the distance increase between these two groups more the inductive effect of the alcohol group decrease and the basicity of the nitrogen site increase.

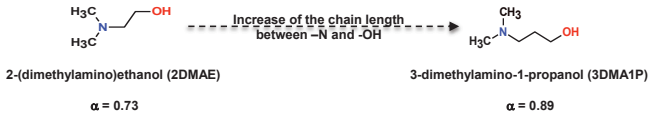

Fig. 4. Modification of the carbon chain length from 2DMAE to 3DMA1P.

Another effect of the amine structure into the absorption of CO_2 is to have an additional nitrogen in the molecule and the increase of the carbon chain length between the two nitrogen (Fig. 5). In comparison with all amines studied in this work, DAP and HMD display the highest CO_2 loading which is up to 1 mole CO_2/mole (1.23 to 1.35 mole CO_2/mole amine respectively). Additionally, HMD, where the two nitrogen are separated by six carbon have the highest CO_2 absorption. More the distance between two nitrogen is high, more the influence between them is reduced and more CO_2 is absorbed.

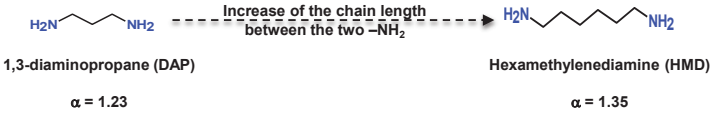

Fig. 5. Presence of two nitrogen in the molecule and modification of the carbon chain length.

The screening results from the absorption of CO_2 by using S.S.S. equipment identify that amines which contain a carbon group (methyl, ethyl or t-butyl) attached to the nitrogen or near it have a high CO_2 loading. Moreover, the effect of alcohol group decrease the CO_2 absorption of the amine if this group is near the nitrogen site. Additionally, in this study, the presence of two nitrogen in the molecule increase the CO_2 absorption. The results indicate that eight amines can be considered for CO_2 absorption: AMP, 2TBAE, 2DMAE, DEEA, SBA, 3DMA1P, DAP and HMD.

3.2. Heat of absorption of CO_2

Determination of the heat of absorption (kJ/mole of CO_2) has been done at 313.15K and atmospheric pressure and presented in Table 2. Fig. 3 shows the experimental data of the heat of absorption obtained from micro-reaction calorimeter for the eight amines determine by the CO_2 absorption screening in addition of MEA and MDEA.

Table 2. Heat of absorption of CO_2 in aqueous amine solution 30wt% at 313.15 K at atmospheric pressure.

	Amine solution	Concentration (wt%)	α_{CO2}	Heat of absorption ΔH (kJ/mole of CO_2)
1	Monoethanolamine (MEA)	30	0.59	- 85.13
2	N-methyldiethanolamine (MDEA)	30	0.74	-52.51
3	2-amino-1-methyl-2-propanol (AMP)	30	0.78	- 80.91
4	2-(tert-butylamino)ethanol (2TBAE)	30	0.79	-80.58
5	2-(dimethylamino)ethanol (2DMAE)	30	0.77	-63.26
6	N,N-diethylethanolamine (DEEA)	30	0.83	-73.17
7	Sec-butylamine (SBA)	30	0.67	-96.67
8	3-dimethyl-amino-1-propanol (3DMA1P)	30	0.85	-54.55
9	1,3-diaminopropane (DAP)	30	1.03	-97.23
10	Hexaméthylènediamine (HMD)	30	1.18	-98.39

In order to evaluate the accuracy of the calorimeter, the heat of absorption of CO_2 of MEA and MDEA 30wt% at 313.15K and atmospheric pressure was measured and compared with the available literature data [18 - 19]. In this work, values of -85.13 kJ/mole of CO_2 (α_{CO2}=0.59) and -52.51 kJ/mole of CO_2 (α_{CO2}=0.74) have been determined for MEA and MDEA, respectively, with 2% uncertainty. These results are in good agreement with the literature data.

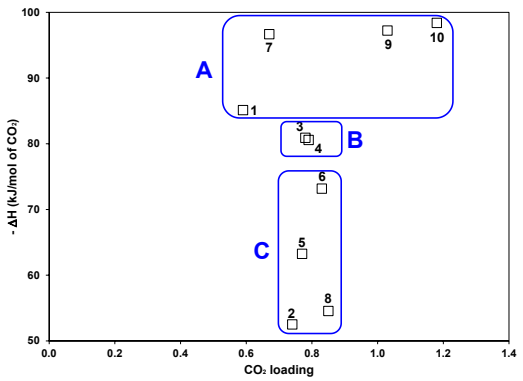

Fig. 3. Heat of absorption ΔH (kJ/mole of CO_2) of aqueous amines solution at 313.15 K and atmospheric pressure. (1) MEA, (2) MDEA, (3) AMP, (4) 2TBAE, (5) 2DMAE, (6) DEEA, (7) SBA, (8) 3DMA1P, (9) DAP, (10) HMD.

Fig. 3 shows that SBA, DAP and HMD have the highest heat of absorption with -96.67 kJ/mole CO_2 (α_{CO2}=0.67), -97.23 kJ/mole CO_2 (α_{CO2}=1.03) and -98.39 kJ/mole CO_2 (α_{CO2}=1.18), respectively. MDEA and 3DMA1P have the lowest heat of absorption with -52.51 kJ/mole CO_2 (α_{CO2}=0.74) and -54.55 kJ/mole CO_2 (α_{CO2}=0.85). According to experimental data, the amines can be classified into three main categories: A, B, and C. The type A includes the primary amines which have the highest heat of absorption. The type B contains the sterically hindered amines and the type C is the tertiary amines. The type A include MEA, SBA, DAP and HMD in which MEA has the lowest heat of absorption, DAP and HMD have the highest CO_2 loading (α=1.03 and 1.18). The type B includes AMP and 2TBAE with a CO_2 absorption capacity higher than MEA and SBA and the heat of absorption lower (-73.17 to -80.91

kJ/mole CO_2). The amines from the type C (MDEA, 2DMAE, DEEA and 3DMA1P) have low heat of absorption in comparison with the amines from the type A and B. Compared to MDEA, 2DMAE and 3DMA1P, DEEA show high heat of absorption of CO_2. This result could be due to the structure of this amine which contains two ethyl group attached to the nitrogen site whereas 2DMAE and 3DMA1P has two methyl group. 2DMAE and 3DMA1P can be considered as a good potential for CO_2 absorption in term of CO_2 loading and the enthalpy of absorption.

3.3. Determination of the kinetics of absorption of CO_2 by aqueous amine solution

The kinetics of the reaction of MEA, AMP, MDEA, 2DMAE and 3DMA1P with CO_2 were measured for the temperature ranging from 298.15 to 313.15K and concentration ranging from 5 to 800 $mol.m^{-3}$ using the stopped-flow technique. The pseudo first-order reaction kinetics (k_0, s^{-1}) of 2DMAE and 3DMA1P are compared with the conventional amines based solvents (MEA, AMP and MDEA).The pseudo first-order rate constants (k_0, s^{-1}) values obtained against amine concentration are given in appendix A (A.2 to A.6).

Fig. 4 illustrates the observed pseudo first-order rate constants (k_0, s^{-1}) plotted against the amine concentration ($mol \cdot m^{-3}$) at 313.15 K. The constant (k_0, s^{-1}) increases with amine concentration. Results show MEA has the highest kinetics compared to all amine studied. The pseudo first-order rate constants of AMP are lower than MEA but higher than the tertiary amines. Comparing the values of the experimental results of the three tertiary amines (MDEA, 2DMAE and 3DMA1P) show that 3DMA1P have the highest kinetics. 3DMA1P has one more carbon in the chain length than 2DMAE and this difference in the structure can alters the kinetic properties and increase it.

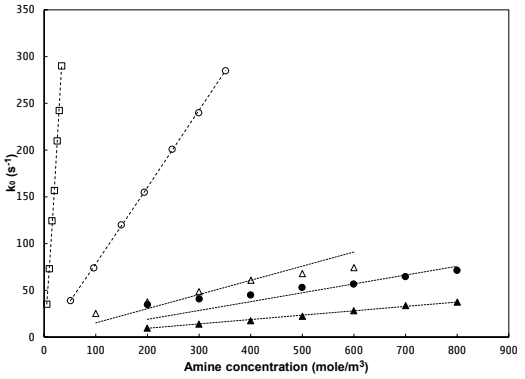

Fig. 4. Pseudo first order rate constants k_0 (s^{-1}) at 313.15 K and different concentrations. (□) MEA, (○) AMP, (Δ) 3DMA1P, (●) 2DMAE, (▲) MDEA, (− − −) zwitterion mechanism, (⋯) based-catalysis mechanism.

Different mechanisms have been proposed in order to interpret the experimental data of the kinetics reaction between aqueous amine solution and CO_2. Zwitterion and thermolecular mechanisms have been proposed to explain the reaction rate of CO_2 with primary or secondary amine and based-catalysis mechanism has been proposed for tertiary amine reaction with CO_2 [20-34]. The zwitterion mechanism is commonly used to describe the reaction mechanism between primary/secondary amines solution and CO_2 and therefore, this model was chosen to investigate the reaction kinetics [20-21]. As shown in Fig. 4, the results obtained for primary or secondary amines (MEA and AMP) indicates that the correlation between the experimental pseudo first-order rate constants with the pseudo first-order rate constants from zwitterion mechanism are good. For the tertiary amines (2DMAE, 3DMA1P and MDEA), the pseudo first-order rate constants from the base-catalysis mechanism are in good agreement with the experimental

pseudo first-order rate constants (Fig. 4). The calculated second order reaction rate constant (k_2, $m^3.mol^{-1}.s^{-1}$) from the zwitterion and based-catalysis mechanisms for each aqueous amines solutions are given in Table 3. The second order rate constants increase with temperature and varied as this order: MEA>AMP>3DMA1P>2DMAE>MDEA.

Table 3. Second order rate constants (k_2, $m^3.mol^{-1}.s^{-1}$) of the aqueous amines solution with CO_2.

T (K)	(k_2, $m^3.mol^{-1}.s^{-1}$)				
	MEA	AMP	MDEA	2DMAE	3DMA1P
298.15	4.796	0.407	0.017	0.032	0.037
303.15	6.355	0.521	0.026	0.050	0.068
308.15	8.343	0.661	0.031	0.071	0.106
313.15	10.859	0.833	0.047	0.095	0.152

The temperature dependency of the second order reaction rate constant (k_2, $m^3.mol^{-1}.s^{-1}$) is correlated with the Arrhenius equation (Eq. (3)).

$$k_2 = A_1.\exp(-\frac{E_A}{RT}) \quad (3)$$

A_1 is the Arrhenius constant ($m^3.mol^{-1}.s^{-1}$), E_A is the activation energy ($kJ.mol^{-1}$) and R is the molar gas constant (8.314 $J.mol^{-1}.K^{-1}$). The temperature dependency of the Arrhenius relation of the aqueous amines solution studied are done and presented in appendix A.2 to A.6. The activation energy from the Arrhenius equation was presented in Table 3 and the $\ln(k_2)=f(1/T(K))$ relation is plotted in appendix A.7.

Table 3. Activation energy E_A ($kJ.mol^{-1}$) of aqueous amines solutions

Amines	Activation energy E_A ($kJ.mol^{-1}$)
MEA	42.28
AMP	37.02
MDEA	50.03
2DMAE	55.71
3DMA1P	72.71

The activation energy E_A ($kJ.mol^{-1}$) calculated from the Arrhenius relation of aqueous AMP solution is the lowest and aqueous 3DM1AP solution is the highest. It can be observed the activation energy for 2DMAE and 3DMA1P is higher than the conventional aqueous amines solution studied in this work.

The results show that 2DMAE and 3DMA1P have a high kinetics in comparison with MDEA and lower than MEA or AMP. In order to improve the kinetics, blended of these two tertiary amines with MEA or AMP can be realized with a reasonable absorption of CO_2 and heat of absorption.

4. Conclusions

This present work investigated new amine-based solvents for CO_2 removal. An evaluation of the absorption capacity, heat of absorption and kinetics between aqueous amine solution and CO_2 was done.

2DMAE and 3DMA1P, tertiary amines, show a good potential for acid gas removal application with respect to CO_2 absorption and heat of absorption. In addition, these two amines are compared with MEA, AMP and MDEA in term of reaction kinetics with CO_2. Second order reaction rate constants k_2 ($m^3.mol^{-1}.s^{-1}$) obtained for 2DMAE and 3DMA1P are higher than MDEA but lower than MEA and AMP. The obtained results indicated that 2DMAE and 3DMA1P have the potential to be used with primary (MEA) and secondary (AMP) amines in order to enhance the CO_2 absorption capacity and the kinetics substituting MDEA.

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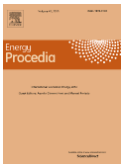

Biography

Dr. Abu Zahra is an associate professor in Chemical Engineering at Masdar Institute of science and technology. Prior to joining Masdar, he worked for the IEA Greenhouse Gas R&D Programme (IEAGHG) and the Dutch research institute (TNO). His current research focuses on CO_2 capture technologies; he is leading the Siemens-Masdar Institute CCS collaboration and the coordinator of the CCS research activities within Masdar Institute. He is a member of the reviewing panel and steering committees for different journals and conferences in his area of expertise.

Appendix A.

A.1. Amines studied in this work

Table A.1. Amines table

	Amines	Abbreviations	Molecular weight ($g.mol^{-1}$)	Supplier	CAS
1	Monoethanolamine	MEA	61.08	Sigma-Aldrich	141-43-5
2	1-amino-2-propanol	1A2P	75.11	Sigma-Aldrich	78-96-6
3	2-amino-1-butanol	2A1B	89.14	Sigma-Aldrich	96-20-8
4	2-amino-1-methyl-2-propanol	AMP	89.14	Sigma-Aldrich	124-68-5
5	2-(tert-butylamino)ethanol	2TBAE	117.19	Sigma-Aldrich	4620-70-6
6	2-(dimethylamino)ethanol	2DMAE	89.14	Sigma-Aldrich	108-01-0
7	N,N-diethylethanolamine	DEEA	117.19	Sigma-Aldrich	100-37-8
8	N-methyldiethanolamine	MDEA	119.16	Sigma-Aldrich	105-59-9
9	Triethanolamine	TEA	149.19	Sigma-Aldrich	102-71-6
10	Sec-butylamine	SBA	73.14	Sigma-Aldrich	13952-84-6
11	Isobutylamine	IBA	73.14	Sigma-Aldrich	78-81-9
12	3-dimethyl-amino-1-propanol	3DMA1P	103.16	Sigma-Aldrich	3179-63-3
13	1,3-diaminopropane	DAP	73.12	Sigma-Aldrich	109-76-2
14	Hexaméthylènediamine	HMD	116.20	Sigma-Aldrich	124-09-4

A.2. Experimental kinetics data for (MEA+CO_2+H_2O) system

Table A.2. Pseudo first-order rate constant k_0 (s^{-1})

Concentration ($mol.m^{-3}$)		Pseudo first-order rate constant k_0 (s^{-1})			
MEA	H_2O	T/K			
		298.15	303.15	308.15	313.15
5.03	55501.50	15	19	27	35
9.83	55485.20	33	41	53	73
14.90	55468.02	48	66	89	124
19.64	55451.92	64	90	119	157
25.14	55433.29	90	122	162	210
29.19	55419.55	108	140	189	242
33.77	55404.01	128	170	226	290

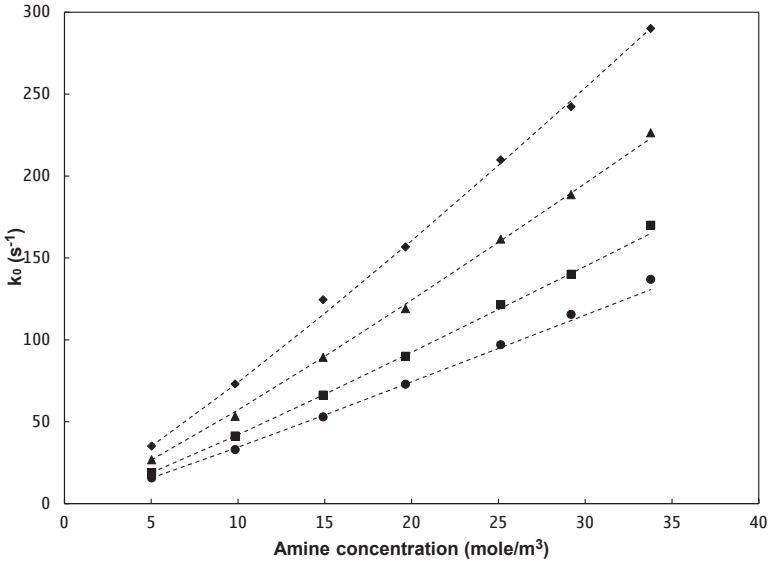

Fig. A.2. Pseudo first order rate constants k_0 (s^{-1}) at 298.15K (●), 303.15K (■), 308.15K (▲) and 313.15 K (♦) and concentration range [5 - 35 mol.m^{-3}] for MEA. (− − −) zwitterion mechanism.

$$k_2(m^3.mol^{-1}.s^{-1}) = 1.228 \times 10^8 * exp\left(-\frac{5085.9}{T}\right)$$

A.3. Experimental kinetics data for (AMP+CO_2+H_2O) system

Table A.3. Pseudo first-order rate constant k_0 (s^{-1})

Concentration (mol.m^{-3})		Pseudo first-order rate constant k_0 (s^{-1})			
AMP	H_2O	T/K			
		298.15	303.15	308.15	313.15
50.79	55267.18	17	22	30	39
95.86	55044.14	32	43	58	74
149.24	54779.98	55	71	93	120
193.67	54560.07	70	101	125	155
247.79	54292.25	95	123	164	201
299.12	54038.22	120	152	194	240
351.05	53781.23	138	176	234	285

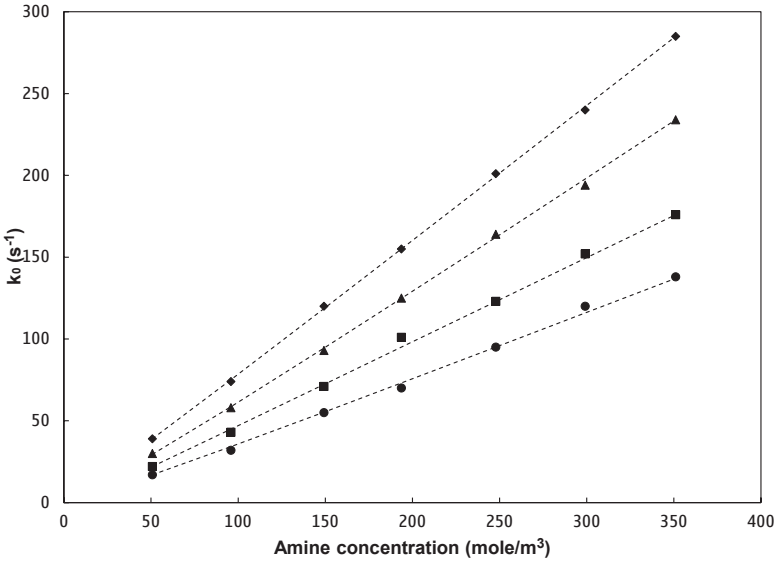

Fig. A.3. Pseudo first order rate constants k_0 (s^{-1}) at 298.15K (●), 303.15K (■), 308.15K (▲) and 313.15 K (♦) and concentration range [50 - 350 mol.m^{-3}] for AMP. (− − −) zwitterion mechanism.

$$k_2(m^3.mol^{-1}.s^{-1}) = 1.249 \times 10^6 * exp\left(-\frac{4453.2}{T}\right)$$

A.4. Experimental kinetics data for (MDEA+CO_2+H_2O) system

Table A.4. Pseudo first-order rate constant k_0 (s^{-1})

Concentration (mol.m^{-3})		Pseudo first-order rate constant k_0 (s^{-1})			
MDEA	H_2O	T/K			
		298.15	303.15	308.15	313.15
199.54	54198.45	4	6	7	10
299.77	53535.39	5	8	12	14
399.83	52873.42	7	10	12	17
500.21	52209.33	9	13	16	22
599.66	51551.41	10	15	19	28
700.23	50886.1	12	18	22	34
800.08	50225.54	14	19	24	37

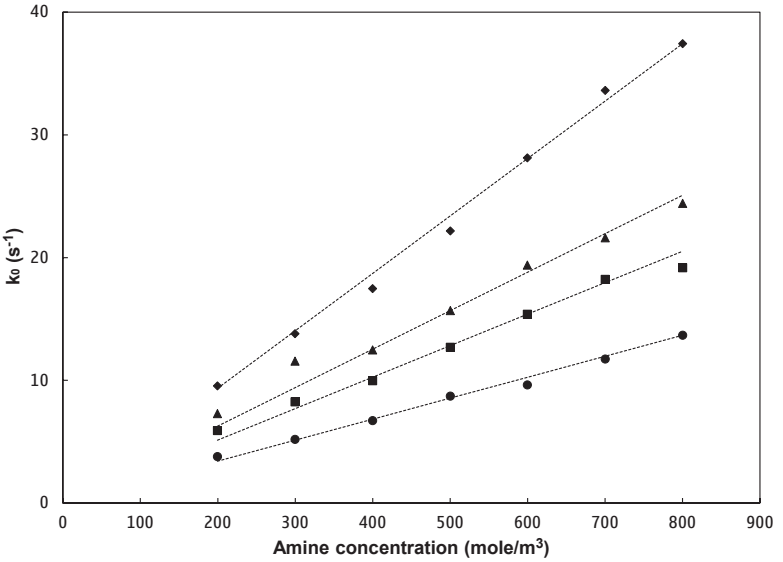

Fig. A.4. Pseudo first order rate constants k_0 (s^{-1}) at 298.15K (●), 303.15K (■), 308.15K (▲) and 313.15 K (♦) and concentration range [200 - 800 mol.m^{-3}] for MDEA. (····) based-catalysis mechanism.

$$k_2(m^3.mol^{-1}.s^{-1}) = 1.01 \times 10^7 * \exp\left(-\frac{6017.8}{T}\right)$$

A.5. Experimental kinetics data for (2-dimethylaminoethanol+CO_2+H_2O) system

Table A.5. Pseudo first-order rate constant k_0 (s^{-1})

Concentration (mol.m^{-3})		Pseudo first-order rate constant k_0 (s^{-1})			
2-dimethylaminoethanol	H_2O	T/K			
		298.15	303.15	308.15	313.15
199.92	54529.15	8	13	21	35
300.06	54033.56	11	18	26	41
399.59	53541.00	13	22	31	45
499.27	53047.72	16	25	36	53
599.16	52553.35	18	30	41	57
699.41	52057.24	20	35	47	65
799.44	51562.18	22	39	54	71

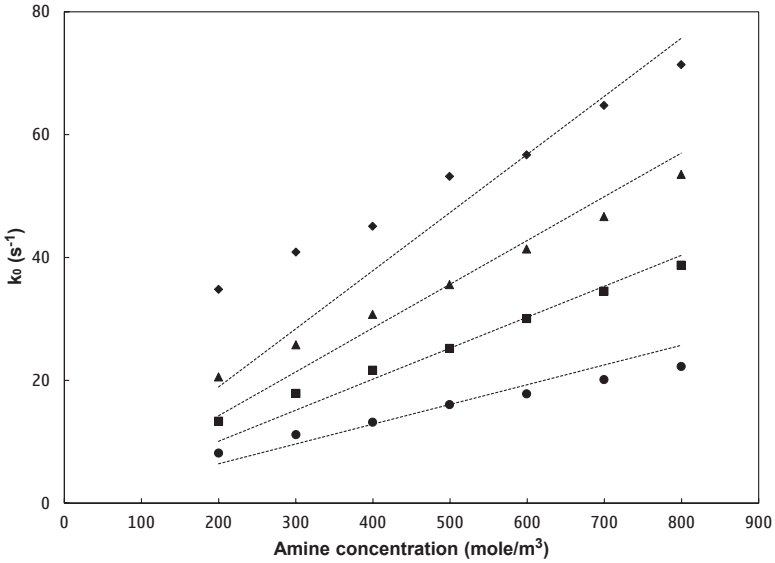

Fig. A.5. Pseudo first order rate constants k0 (s-1) at 298.15K (●), 303.15K (■), 308.15K (▲) and 313.15 K (♦) and concentration range [200 - 800 mol.m^{-3}] for 2-dimethylaminoethanol. (····) based-catalysis mechanism.

$$k_2(m^3.mol^{-1}.s^{-1}) = 1.92 \times 10^8 * exp\left(-\frac{6700.7}{T}\right)$$

A.6. Experimental kinetics data for (3-dimethylamino-1-propanol+CO_2+H_2O) system

Table A.6. Pseudo first-order rate constant k_0 (s^{-1})

Concentration (mol.m^{-3})		Pseudo first-order rate constant k_0 (s^{-1})			
3-dimethylamino-1-propanol	H_2O	T/K			
		298.15	303.15	308.15	313.15
99.84	54946.73	7	11	16	25
199.98	54373.22	10	17	27	38
299.95	53800.63	12	21	34	49
400.54	53224.52	15	27	42	59
500.04	52654.65	18	32	49	65
599.95	52082.47	22	36	53	74

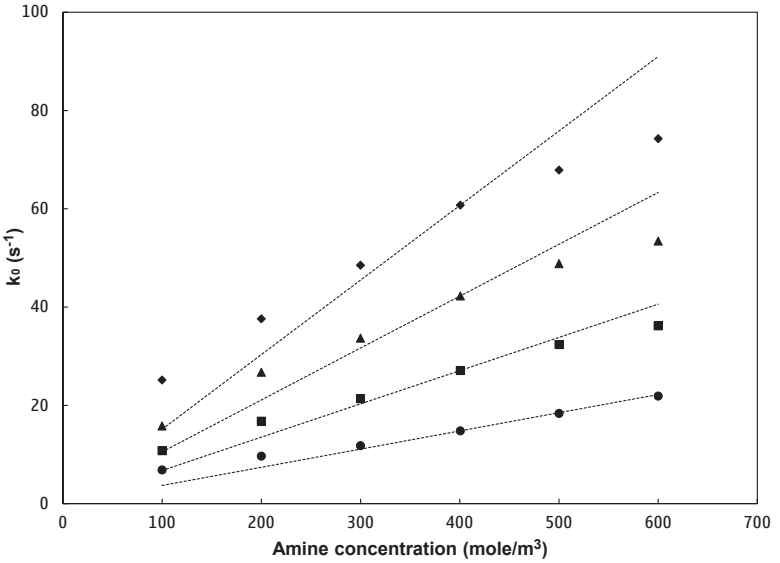

Fig. A.6. Pseudo first order rate constants k0 (s-1) at 298.15K (●), 303.15K (■), 308.15K (▲) and 313.15 K (♦) and concentration range [200 - 800 mol.m^{-3}] for 3-dimethylamino-1-propanol. (····) based-catalysis mechanism.

$$k_2(m^3.mol^{-1}.s^{-1}) = 2.14 \times 10^{11} * exp\left(-\frac{8745.2}{T}\right)$$

A.7. Comparison of Arrhenius relation: lnk_2=f(1/T(K))

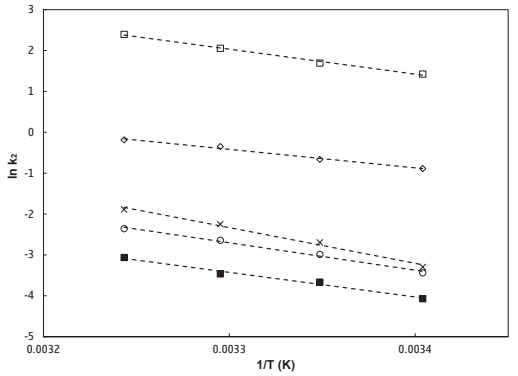

Fig. A.7. Comparison of the relation lnk_2=f(1/T(K)) in a temperature range of (298.15-313.15 K) for MEA (□), AMP (◊), 3DMA1P (×), 2DMAE (○) and MDEA (■).